

## Grazing Angle Infrared Spectroscopy of Chromate Conversion Coatings

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Beamline(s): U10B

**Introduction:** Dichromate based solutions have been used as corrosion inhibitors on aluminum since the beginning of the last century (1,2). Since then, the mechanism of protection offered by chromate-based solutions has been under investigation. Toxicity and mutagenic effects of hexavalent chromium have stimulated the development of alternative coatings (3-4), the success of which depends on understanding precisely the underlying mechanism of protection offered by hexavalent chromium. The ability of Fourier transform infrared spectroscopy to be operated in various modes makes it a very attractive analytical technique.

**Methods and Materials:** Polished AA2024-T3 (1 $\mu$ m finish, Cu-free polishing solution) samples were conversion coated using Alodine 1200S® (Parker Amchem) for 300 seconds. The samples were rinsed thoroughly in de-ionized water followed by drying with nitrogen. Infrared spectra were collected at UV beamline U10B using a Thermo-Nicolet FT-IR Continuum microscope in both grazing angle (GAIRS) and near normal reflection-absorption (RAIRS) modes.

**Results:** Figs. 1 & 2 show the spectra obtained from RAIRS and GAIRS modes respectively. The strong and broad absorption band centered around 3600-3000  $\text{cm}^{-1}$  is due to both OH stretching and water of crystallization (5). The sharp spectral feature observed at  $\sim 2080 \text{ cm}^{-1}$  is due to the C-N stretching mode from the  $\text{Fe}(\text{CN})_6^{3-}$ . Chromate conversion coatings contain a significant amount of cyanide. HOH bending of lattice water is observed at  $\sim 1620 \text{ cm}^{-1}$ . A very weak absorption due to organic amines may also be seen centered around 1410  $\text{cm}^{-1}$ . Absorption due to hexavalent chromate and dichromate occurring at  $\sim 920$ -950  $\text{cm}^{-1}$  and  $\sim 820$ -840  $\text{cm}^{-1}$  corresponding to Cr(VI)-O vibration are also labeled. All the above spectral features are routinely observed on CCCs and are discussed elsewhere (6-8). A spectral feature is also observed  $\sim 605$ -607  $\text{cm}^{-1}$  especially using the GAIRS method of analysis. We believe this band to be due to  $\text{Cr}_2\text{O}_3$  as reported by Guillaumet et al. (9).

It is observed from the spectra that the GAIRS method is more sensitive to the surface coating than the RAIRS method of analysis. This is clearly seen in the case of spectral features due to Cr(VI)-O vibration ( $\sim 920 \text{ cm}^{-1}$ ), HOH bending of lattice water (1620  $\text{cm}^{-1}$ ) and the feature at  $\sim 606 \text{ cm}^{-1}$ . Also the signal to noise ratio is higher in case of the GAIRS as can be seen from the high quality spectrum near the lower wavenumbers. In fact the spectral feature at 606  $\text{cm}^{-1}$  is almost masked in the reflection-absorption mode by the noise around that feature. Table 1 provides a comparison of peak heights as observed in each spectrum. The peak heights are then normalized with respect to the broad 3300  $\text{cm}^{-1}$  feature due to OH stretching. The peak heights have been used for comparison over peak area, as peak areas are dependent on peak width and may lead to erroneous results in case of peak width broadening as observed in case of the feature due to OH stretching. Table 1 indicates that the sensitivity can be increased by nearly an order of magnitude by the use of GAIRS as compared to the standard reflection-absorption method of analysis.

**Conclusions:** The sensitivity to chromate using a grazing angle objective was observed to increase by nearly an order of magnitude when compared to near-normal reflection-absorption infrared spectroscopy mode. Hence synchrotron radiation based grazing angle infrared spectroscopy can prove to be a highly effective tool in studying the local speciation or chemistry of surfaces under ambient conditions.

**Acknowledgments:** The U.S. Air Force Office of Scientific Research under contract F4962093-1-0218 supported this work. Lt. Col. Paul Trulove, Ph.D. served as contract officer. NSLS is supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886. We thank Lisa Miller and Nebojsa Marinkovic for discussions.

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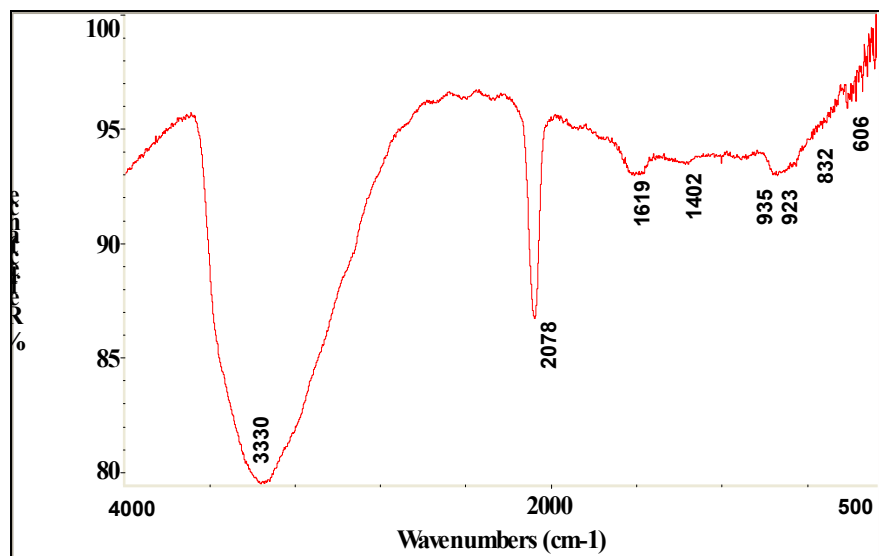


Fig 1. FT-IR spectrum of a chromate conversion coating obtained using reflection-absorption mode.

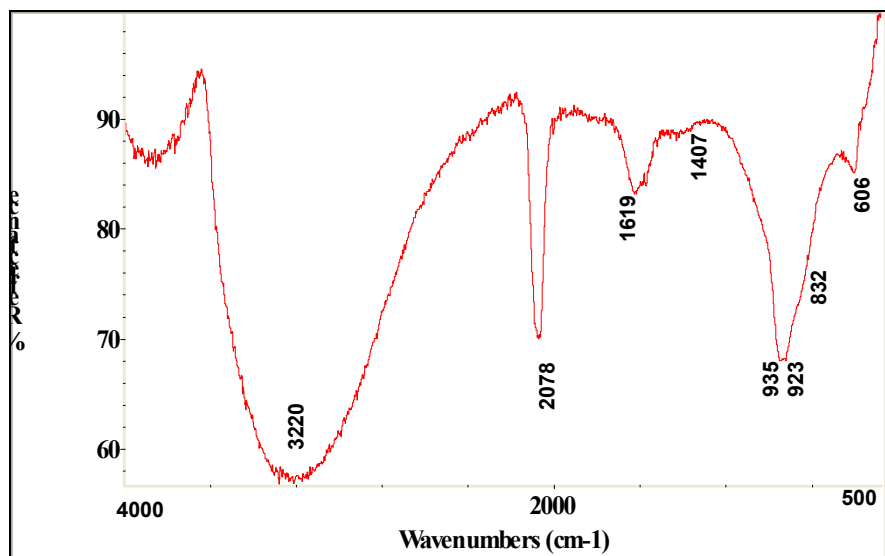


Fig 2. FT-IR spectrum of a chromate conversion coating obtained using grazing-angle mode.

Band	Normal Reflectance	Normalized w.r.t. H <sub>2</sub> O	Grazing Angle	Normalized w.r.t. H <sub>2</sub> O	Ratio of Grazing Angle /Normal Reflectance
H <sub>2</sub> O	16.16	1.000	35.73	1.000	1.00
CN <sup>-</sup>	8.68	0.537	20.04	0.561	1.04
OH <sup>-</sup>	0.91	0.056	5.673	0.158	2.82
CrO <sub>4</sub> <sup>2-</sup>	0.95	0.059	19.44	0.544	9.22
606	0.29	0.018	2.898	0.081	4.50

Table 1: Peak heights, normalized peak heights and ratio of peak heights obtained by RAIRS and GAIRS techniques.